

Development and characterization of material structures prepared by different physical and chemical vapor deposition methods

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Introduction and Objectives

For the development of different materials it is a very important step to develop production technology and to understand their formation processes. The aim of my experimental work was to study the formation mechanisms of different structures grown in vacuum or low gas pressure and to clarify the questions left open in the literature in case of these materials. I have studied and explained the following problems as a function of production parameters. First, the development of layers with elementary composition (3D Ni and 2D graphene). Second, the formation of compound AlN layers. The last part of my theses shows in the phase separation in CrN/Si₃N₄ composite layers. In the case of graphene deposited on <111> oriented Ni substrate it was not clear how the existence of nickel domains / grains rotated around the <111> axis can affect the growth, quality and faults of graphene, and how are these influenced by the grow parameters. Similarly, it was an open question, how we can control the formation and size of the developed turbostratic carbon with the experimental parameters during the graphene deposition on {111} Ni grown on a sapphire substrate, and how we can determine their formation above the defects found in the nickel substrate. Several different results and various models are present in the literature for AlN growth as a function of the preparation procedure. I tried to sort out these changes with a systematic variation of the pressure. I clarified the question of CrN/Si₃N₄ layers if it is possible to form a fine nanostructure (3D nanocomposite) with a composition completely different from that known at super-hard materials.

To achieve my goal, several structural analysis methods were used (in addition to methods of production). For the investigated 3D materials the experimental methods (TEM, HRTEM, EFTEM, AFM, STM, XRD, SEM/EBSD) available in our country were sufficient to perform the investigations. However for studying the atomic arrangements in 2D graphene Cs-corrected HRTEM was also used, which is only available (with scholarship) abroad at the moment.

The first known 2D material which is stable at room temperature is graphene. Several methods have been developed for the production of high-quality defect-free graphene for electronic application, however this problem has not been completely resolved. One of the most promising methods of preparation could be vapor deposition of carbon from methane to copper substrate. The advantage of copper substrate is that it is a good catalyser, which means that a large proportion of methane decomposes on the copper surface about 900°C temperature. Another important feature with respect to the graphene growth is that copper does not dissolve the carbon. As a result, the carbon decomposed from the methane remains

on the surface of the substrate and after the formation of a single layer of graphene the methane decomposition process stops, because the graphene is a much worse catalyst than the copper. Due to that the growth of graphene on the copper surface is a self-regulating process. However, the copper substrate has two disadvantages. First, the Cu melting temperature is close to the deposition temperature, so the surface can be corrugated. Second, grain boundaries can be formed in the graphene, because difficult to control the orientation of the graphene. Another commonly used metal substrate for graphene deposition is nickel. On this substrate it is much more difficult to form single layer graphene, because Ni dissolves carbon atoms at the conventional deposition temperatures. However, its melting point is higher than copper and the graphene lattice can be fitted well to the Ni {111} plane. Single layer graphene could be grown only on single crystal nickel (not on polycrystalline nickel because at grain boundaries more carbon is solved than at the bulk and during the cooling period more carbon dissolved to substrate surface and at these areas graphite or turbostratic carbon might be formed). The orientation relationships between the nickel {111} and the graphene were studied predominantly with LEED in the literature. The LEED study was significantly affected by the presence of turbostratic carbon, so it could not fully confirm the existence of the epitaxial grow between the nickel {111} and the graphene if turbostatic carbon was also formed. For the formation of thicker turbostratic carbon the twin boundaries in the nickel substrate were suspected, however this was not proved experimentally. In the present dissertation the orientation relationship between the Ni {111} and the graphene were examined under conditions where usually turbostratic carbon formation was observed in the literature. It was shown that coherent single layer graphene can be grown in several μm^2 area in such conditions. In my work, another aim was to examine the relationship between the formation of turbostratic carbon and the structural defects in the nickel {111} substrate.

For graphene deposition, $\langle 111 \rangle$ oriented nickel substrates produced in different ways were used in the literature. The use of single-crystal nickel is too expensive, so other single crystal substrates are used to grow thin layers nickel for graphene growth. Single crystal sapphire {0001} is one of the substrates, which are preferred to grow nickel with $\langle 111 \rangle$ orientation, due to the 4-9% misfit between the Ni {111} and the sapphire {00001} planes. However, the exact orientation relationships between the sapphire and the nickel were not investigated. The surface morphology of the nickel layer deposited on a sapphire {0001} substrate is very diverse as observed by AFM in the literature. There are observations of 30-70 nm pits on the surface of the nickel and 30-40 nm deep trenches are also observed. The formation of this diverse surface morphology is poorly investigated or based only on assumptions. Cross-

sectional samples have not been studied to understand the problem and to confirm the assumptions. In my dissertation the investigation of the orientation relationship between the nickel {111} layer and the sapphire {0001} substrate are shown, and the mechanism of the development of different orientations is discussed. The diverse surface morphologies, also observed in the literature, were studied in cross-sectional TEM specimens and the reasons of their formation were identified.

The use of the nitrides has a wide variety. One application could be the super-hard coatings. To develop superhard composites, two-phase nanocomposite system should be grown with thin crystalline grains with the diameter of a few nanometers in an amorphous matrix. For the hardest composites it was assumed, that only monolayer thick amorphous (Si-N) layer separates the crystalline (typically TiN) particles. In other hard layers Cr was used instead of the Ti. In the case of superhard titan nitride composites it was important to get a proper structure by using oxygen-free target, this makes very difficult to manufacture these types of layers. Other, less expensive, simpler, easier to use industrial methods are under development, for that, it is important to understand the structure and formation of this new composite materials. Based on previous studies of the Cr-Si-N system, the maximum hardness was reached at 2-3 at.% Si content. The phase separation between the amorphous Si-N and crystalline CrN has not been shown experimentally. We achieved a similar (though not super) hardness with significantly higher Si ratios by sputtering from sintered Cr-Si targets. In the dissertation I show the experimental proof of the phase separation of these layers.

In addition to the application as super-hard materials, nitrides (for example AlN) also have numerous other uses and there may be new areas too. For the widest range of use it is also necessary to be able to produce structures with different phases although with the same composition. In my dissertation, structure and formation mechanism are studied in thin layers prepared by various methods as a function of a systematic set of parameters.

The dissertation begins with a literature summary about the production of graphene, the growth of <111> oriented nickel layers on single crystal sapphire and about hard composite coatings and the growth of the observed AlN metastable cubic phase. This is followed by a general description of the techniques used during the growth processes and the examination methods applied in my work. My own results are in section 5, which is divided into four major parts:

- Ni sputtering onto single crystal sapphire substrate
- Preparation and characterization of graphene grown on {111} nickel surface
- Structural study of AlN thin layers formed by Pulsed laser deposition

- Investigation of CrN/Si₃N₄ nanocomposite structures.

In the first subchapters of each of the four parts the growth conditions of the layers and the methods applied in the investigation are summarized. In the following subchapters, the results are presented, and in last subchapters the results are interpreted and summarized.

Ph.D. Theses

1. a) I showed that the sputtered Ni layer grows epitaxial to the $\langle 0001 \rangle$ oriented sapphire substrate, and the nickel $\{111\}$ planes grow parallel with the sapphire $\{0001\}$ planes. However, two alternative orientation of Ni can grow epitaxial to the sapphire substrate which are rotated to each other with 30° (that can be formulated symmetry equivalently as 90°). Either the $\{110\}$ planes of nickel ("A" orientation) or its $\{211\}$ planes ("B" orientation) can grow parallel to the sapphire $\{30-30\}$ planes.

b) According to my interpretation the "A" type of orientation is energetically favorable in case of thinner layers and in the nucleation period, due to its low interfacial energy, which is lower than the interfacial energy for the "B" orientation. At the "A" orientation the misfit is - 9.29% between the nickel and the sapphire lattice, while in the "B" type orientation it is + 4.68%, which means that the "B" orientation stores less elastic energy, so this orientation will be more favorable in the case of larger crystals or thicker layer. In accordance with this interpretation, my experiments have shown that it is possible to control the emerging orientation with the control of the parameters which influence the nucleation density, the recrystallization and growth subsequent to coalescence and I was able to produce nickel layer with only one orientation (and its twin orientation) [S1].

2. a) I showed that the varied surface morphologies formed on the Ni $\{111\}$ layer sputtered on sapphire $\{0001\}$ plane are caused by the grains with different orientations in the nickel layer. In these layers only two types of grain boundaries are present: the high-energy grain boundaries between the "A" and "B" type orientations which are rotated to each other with 30° and twin boundaries. The 5-40 nm deep trenches always form in such layers over the grain boundaries.

b) The 50-70 nm deep dents formed under special growth conditions (750°C substrate temperature and 5,7 Å/s growth rate) appeared within the single-oriented surface area where a subsurface grain with 100-200 nm lateral extension and the other orientation was overgrown by the dominant orientation. In these layers the rare grains with "B" orientation are located at the sapphire/Ni interface with 100-200 nm lateral size and they are surrounded by grains with "A" orientation. During growth the impurities are swept to the grain boundaries, where they

hinder the growth of the drop-shaped "B" orientated grains. The observed 50-70 nm deep dents were formed due to the time required by the lateral growth, because the Ni atoms are less likely built into the lattice at the area covered with more impurity, and so they are more likely to migrate to cleaner areas [S1].

3. a) I showed that graphene can be grown dominantly epitaxially on nickel {111} surface above 900°C (in contrast to earlier literature) with chemical vapor deposition (CVD) (during the growth argon 1 l/min, hydrogen 3,7 l/min and methane 0,1 l/min gas mixture was used, the deposition was 5 minutes long).

b) Graphite flakes were formed over the graphene during the deposition and the cooling period, if the carbon concentration was sufficiently increased due to the carbon segregated from the nickel to the surface. The carbon concentration can be controlled by the use of hydrogen during the deposition and cooling (with 1,5 l/min of argon and 0,5 liter/min of hydrogen gas mixture, the cooling rate was 16°C/min), which prevents the formation or preservation of the amorphous carbon on the surface of the graphene.

c) Larger and thicker (several nanometer) graphene flakes were formed above the nickel high-energy grain boundaries and the incoherent twin boundaries' high-energy sections where more carbon can be solve into the substrate. It was possible to suppress the formation of smaller flakes (compared with the flakes formed above the high-energy grain boundaries) with the use of appropriate deposition parameters above the defect-free Ni surface with $\langle 111 \rangle$ orientation, as well as above the regular incoherent twin boundaries [S2].

4. I showed that thin layers with three different phases can be grown on a Si {100} substrate by pulsed laser deposition (3 Hz pulse frequency) from AlN target, by systematically varying the nitrogen gas pressure (10^{-4} Pa, 0,1 Pa, 10 Pa). Polycrystalline hexagonal AlN layers were grown in low pressure (10^{-4} Pa) nitrogen gas with the c-axis perpendicular to the substrate surface. Amorphous AlN layer may form in 0,1 Pa nitrogen gas pressure. Amorphous AlN layer with small (4-5 nm) cubic AlN nano particles can be formed in 10 Pa nitrogen gas pressure. The fact that an amorphous layer is grown in the medium pressure can be explained by the energy loss due to the collisions, and by the formation of few atomic clusters in the gas space, while the appearance of metastable cubic particles at high pressure can be attributed to the formation of larger clusters in the gas space [S3, S4].

5. I showed that phase separation can form a two-phase nanocomposite system when a sintered target of 65 at.% Cr and 35 at.% Si (so a dramatically different composition than what is known to produce super-hard materials) is sputtered in nitrogen at 600°C temperature. For this system I was the first to show experimentally that the sputtered layer consists of CrN

crystals with diameter of 5-8 nm separated by a 0,5-2 nm thick amorphous matrix, rich in Si, possibly silicon nitride [S5].

Publications Directly Related to the Ph.D. Theses

- [S1] Zs. Fogarassy, G. Dobrik, L. K. Varga, L. P. Biró, J. L. Lábár; Growth of Ni layers on single crystal sapphire substrates; *Thin Solid Films* 539 (2013) 96–101.
- [S2] Zs. Fogarassy, M. H. Rummeli, S. Gorantla, A. Bachmatiuk, G. Dobrik, K. Kamarás, L. P. Biró, K. Havancsák, J. L. Lábár; Dominantly epitaxial growth of graphene on Ni (111) substrate; *Applied Surface Science* 314 (2014) 490–499.
- [S3] A. Szekeres, Zs. Fogarassy, P. Petrik, E. Vlaikova, A. Cziraki, G. Socol, C. Ristoscu, S. Grigorescu, I. N. Mihailescu; Structural characterization of AlN films synthesized by pulsed laser deposition; *Applied Surface Science* 257 (2011) 5370-5374.
- [S4] S. Bakalova, A. Szekeres, Z. Fogarassy, S. Georgiev, T. Ivanov, G. Socol, C. Ristoscu, I. N. Mihailescu; Synthesis of Nanostructured PLD AlN Films: XRD and Surface-Enhanced Raman Scattering Studies; *Micro and Nanosystems* 6 (2014) 9-13.
- [S5] J. Morgiel, J. Grzonka, R. Mania, S. Zimowski, J. L. Labar, Zs. Fogarassy; Relation between microstructure and hardness of nano-composite CrN/Si₃N₄ coatings obtained using CrSi single target magnetron system; *Vacuum* 90 (2013) 170-175.

Additional Publications

- [E1] Microstructure and mechanical properties of commercial purity HIPed and Crushed Aluminum. Q. H. Bui, G. F. Dirras, A. Hocini, S. Ramtani, A. Abdul-latif, J. Gubicza, T. Chauveau, Z. Fogarassy, *Materials Science Forum* 584-586 (2008) 579-584.
- [E2] Microstructure and mechanical behavior of ultrafine-grained titanium. J. Gubicza, Zs. Fogarassy, Gy. Krállics, J. Lábár, T. Törköly, *Materials Science Forum* 589 (2008) 99-104.
- [E3] Mechanical and microstructural characterization of AL-6082 ultrafine-grained alloys processed by ECAP combined with traditional forming techniques. Gy. Krállics, A. Fodor, J. Gubicza, Zs. Fogarassy, *Materials Science Forum* 589 (2008) 111-116.
- [E4] The effect of impurity level on ultrafine-grained microstructures and their stability in low stacking fault energy silver. Z. Hegedűs, J. Gubicza, M. Kawasaki, N. Q. Chinh, Zs. Fogarassy, T. G. Langdon, *Materials Science and Engineering: A*, 528 (2011) 8694–8699.
- [E5] Microstructure of low stacking fault energy silver processed by different routes of severe plastic deformation. Z. Hegedűs, J. Gubicza, M. Kawasaki, N. Q. Chinh, Zs. Fogarassy, T. G. Langdon, *Journal of Alloys and Compounds* 536, Supplement 1 (2012) S190–S193.

- [E6] Electron diffraction based analysis of phase fractions and texture in nanocrystalline thin films; Part III: Application examples. J.L. Lábár, M. Adamik, B.P. Barna, Zs. Czígány, Zs. Fogarassy, Z.E. Horváth, O. Geszti, F. Misják, J. Morgi, G. Radnóczy, G. Sáfrán, L. Székely and T. Szüts, *Microscopy and Microanalysis* 18 (2012) 406-420.
- [E7] High temperature thermal stability of ultrafine-grained silver processed by equal-channel angular pressing. Z. Hegedus, J. Gubicza, M. Kawasaki, N.Q. Chinh, K. Süvegh, Z. Fogarassy, T.G. Langdon, *Journal of Materials Science* 48 (2013) 1675-1684.
- [E8] The influence of impurity content on thermal stability of low stacking fault energy silver processed by severe plastic deformation. Z. Hegedus, J. Gubicza, M. Kawasaki, N.Q. Chinh, Z. Fogarassy, T.G. Langdon, *Materials Science Forum* 729 (2013) 222-227.
- [E9] Complex study of h-induced structural rearrangements in FeZr glasses. B. Vehovszky, P. Kamasa, J. Kovác, Z. Fogarassy, *Materials Science Forum* 729 (2013) 509-514.
- [E10] Sputtered nanocrystalline ceramic TiC/amorphous C thin films as potential materials for medical applications. N. Oláh, Z. Fogarassy, M. Furkó, C. Balázsi, K. Balázsi, *Ceramics International* 41 (2015) 5863-5871.